

Time-dependent diffusion in tubes with periodic partitions

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The presence of obstacles leads to a slowdown of diffusion. We study the slowdown when diffusion occurs in a tube, and obstacles are periodically spaced identical partitions with circular apertures of arbitrary radius in their centers. The mean squared displacement of a particle diffusing in such a system at large times is given by $\langle \Delta x^2(t) \rangle = 2D_{\text{eff}}t$, $t \rightarrow \infty$, where D_{eff} is the effective diffusion coefficient, which is smaller than the particle diffusion coefficient in the tube with no partitions, D_0 . The latter characterizes the short-time behavior of the mean squared displacement, $\langle \Delta x^2(t) \rangle = 2D_0t$, $t \rightarrow 0$. Thus, the particle diffusion coefficient decreases from D_0 to D_{eff} as time goes from zero to infinity. We derive analytical solutions for the Laplace transforms of the time-dependent diffusion coefficient and the mean squared displacement that show how these functions depend on the geometric parameters of the tube. To obtain these solutions we replace nonuniform partitions with apertures by effective partitions that are uniformly permeable for diffusing particles. Our choice of the partition permeability is based on the recent result for the corresponding effective trapping rate obtained by means of boundary homogenization. To establish the range of applicability of our approximate theory we compare its predictions with the results found in Brownian dynamics simulations. Comparison shows excellent agreement between the two at arbitrary value of the aperture radius when the tube radius does not exceed the interpartition distance. © 2009 American Institute of Physics. [doi:10.1063/1.3224954]

I. INTRODUCTION

Diffusion in tubes of periodically varying geometry has been discussed in quite different contexts including chemical engineering,¹ transport in zeolites,² and man-made periodic porous materials,³ controlled drug release,⁴ transport in soils,⁵ different biological tissues and neurons,⁶ etc. Any periodic variations of the tube cross section lead to a slowdown of diffusion compared to that in a tube of constant cross section. The point is that the broader parts of the tube work as entropy wells that trap diffusing particles. These wells are separated by the entropy barriers, which are formed by the narrow parts of the tube (bottlenecks). As a consequence, the long-time behavior of the mean squared displacement of a particle diffusing along the tube axis (x -coordinate) is given by $\langle \Delta x^2(t) \rangle = 2D_{\text{eff}}t$, where the effective diffusion coefficient, D_{eff} , is below the particle diffusion coefficient in a tube of constant cross section, D_0 . The latter characterizes the short-time behavior of the mean squared displacement, $\langle \Delta x^2(t) \rangle = 2D_0t$ as $t \rightarrow 0$. From here on we use the angular brackets, $\langle \cdots \rangle$, as a notation of the averaging over both the particle stochastic trajectories and its initial positions, which are assumed to be uniformly distributed over the tube. Time-dependent diffusion coefficient, $D(t)$, can be defined as

$$D(t) = \frac{1}{2} \frac{d\langle \Delta x^2(t) \rangle}{dt}. \quad (1)$$

This function monotonically decreases from D_0 to D_{eff} as time goes from zero to infinity. The goal of the theory is to establish the relation between $D(t)$ and the tube geometry. In particular, this includes the relation between D_{eff} and parameters of the tube.

When the tube cross section varies slowly, the entropy effects in diffusion can be analyzed using modified Fick–Jacobs (F-J) equation.⁷ The difference between the regular F-J equation⁸ and its modified version lies in the fact that the former contains D_0 while the latter contains position-dependent diffusion coefficient that depends on the tube geometry.⁸ However, this approach is inapplicable to tubes with periodic partitions considered in the present paper, since here the tube cross section changes abruptly. Partitions separate the tube into identical compartments of length l (Fig. 1). Each partition has a circular aperture of radius a in its center, through which the particle can go from one compartment to the other. To solve the problem, one has to find the particle propagator in the compartments and then match the propagator in the neighboring compartments on the connecting aperture. This task is too difficult to be done. To overcome the difficulties we replace the nonuniform partitions containing apertures by effective uniformly permeable partitions with properly chosen permeability. As a result, the problem re-

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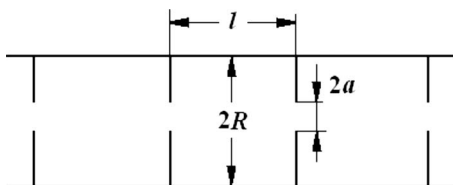


FIG. 1. Representation of a tube of radius R with periodic partitions separated by distance l . Each partition has a circular aperture of radius a in its center.

duces to that of diffusion among periodically spaced uniformly permeable partitions. An exact solution to this problem was obtained recently.⁹ We use this solution to find the Laplace transforms of $\langle \Delta x^2(t) \rangle$ and $D(t)$ as functions of the tube parameters.

The outline of the present paper is as follows. In the next section we explain our choice of the effective permeability of the partitions as a function of D_0 and radii R and a of the tube and the aperture. This choice is based on a version of the effective medium approximation called boundary homogenization.¹⁰ In this section we also discuss the dependence of D_{eff} obtained using the Crick formula on the tube parameters. In addition, we compare D_{eff} predicted theoretically and found numerically in Brownian dynamics simulations. An alternative derivation of the formula for D_{eff} has been reported recently.¹¹ Transient behavior of the diffusion coefficient is discussed in Sec. III. In this section we also compare $\langle \Delta x^2(t) \rangle$ obtained in Brownian dynamics simulations and found by numerically inverting the Laplace transform predicted by the theory. Comparison shows that theoretically predicted dependences $\langle \Delta x^2(t) \rangle$ perfectly agree with the simulation results when the tube radius does not exceed the interpartition distance. In the concluding section we summarize the results obtained in the paper and discuss the conditions of applicability of boundary homogenization that is used when deriving these results.

II. EFFECTIVE DIFFUSION COEFFICIENT

In this section we first discuss the choice of the effective permeability. Then we use this permeability to find D_{eff} and to analyze its dependence on the tube parameters. First, we note that a particle located in an aperture escapes to each of the two compartments connected by the aperture with equal probability, $1/2$. Therefore, the effective permeability, P , is equal to $\frac{1}{2}$ of the “trapping” rate of the particles diffusing in the compartment by the aperture, i.e., by a circular absorbing disk of radius a located in the center of the otherwise reflecting partition. Denoting this trapping rate by κ , we can write $P = \kappa/2$. Thus, finding of the effective permeability reduces to finding of the trapping rate.

An approximate solution for the trapping rate was recently obtained by means of boundary homogenization.¹⁰ The result is¹⁰

$$\kappa = \frac{4D_0}{\pi R} f(\nu), \quad \nu = \frac{a}{R}, \quad (2)$$

where $f(\nu)$ is a dimensionless function, which monotonically increases with the radii ratio, ν , from unity to infinity as ν

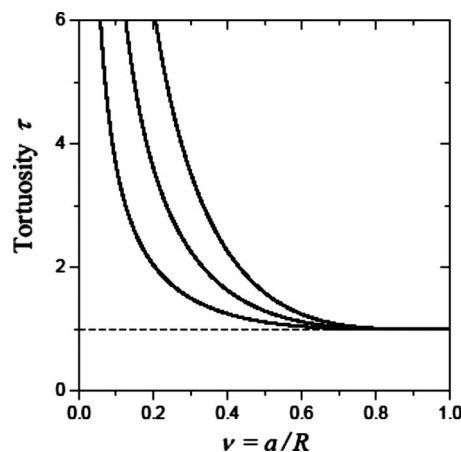


FIG. 2. Tortuosity τ , Eq. (6), as a function of the radii ratio $\nu = a/R$ at three values of the interpartition distance, $l/R = 1, 2$, and 5 from top to bottom. The tortuosity decreases and approaches unity as the interpartition distance increases and grows as the size of the aperture decreases.

grows from zero to unity. As $\nu \rightarrow 0$, $f(\nu)$ tends to unity, and the trapping rate takes the form $\kappa = 4D_0a/(\pi R^2)$, which follows from the Berg–Purcell–Shoup–Szabo theory of trapping by patchy surfaces^{12,13} in the limit of low patch surface fraction.¹⁰ As $\nu \rightarrow 1$, $f(\nu)$ diverges, and κ tends to infinity, since the entire partition becomes a perfectly absorbing trap for diffusing particles that corresponds to the absence of the partitions in the tube. A very accurate approximating formula for $f(\nu)$ was suggested in Ref. 10(a),

$$f(\nu) = \frac{1 + 1.37\nu - 0.37\nu^4}{(1 - \nu^2)^2}. \quad (3)$$

Below we use the relations in Eqs. (2) and (3) when studying D_{eff} as a function of the tube parameters, a , R , and L .

Effective diffusion coefficient of a particle diffusing among periodically spaced permeable partitions is given by¹⁴

$$D_{\text{eff}} = \frac{D_0 Pl}{D_0 + Pl}, \quad (4)$$

where P is the partition permeability and l is the interpartition distance. We can write D_{eff} as

$$D_{\text{eff}} = \frac{D_0}{\tau}, \quad (5)$$

where τ is the tortuosity, which is a fudge factor that accounts for the effect of obstacles on diffusion.¹⁵ Using Eqs. (2) and (4) and the fact that $P = \kappa/2$ we can write the tortuosity in terms of the tube parameters,

$$\tau = 1 + \frac{D_0}{Pl} = 1 + \frac{\pi R}{2l\nu f(\nu)}. \quad (6)$$

In the absence of partitions ($\nu = 1$, $f(\nu) = \infty$) we have $\tau = 1$ and $D_{\text{eff}} = D_0$, as it must be. As $\nu \rightarrow 0$ ($f(\nu) \rightarrow 1$), the tortuosity diverges as $1/\nu$, and D_{eff} tends to zero as $1/a$. As can be expected, the effect of partitions weakens as the interpartition distance, l , increases. The dependence of the tortuosity on ν and l is illustrated in Fig. 2.

To check the accuracy of our approximate theory, which is based on boundary homogenization, we compare D_{eff}

TABLE I. Ratios of the effective diffusion coefficients found in Brownian dynamics simulations to their theoretically predicted counterparts, Eqs. (5) and (6). Majority of the simulation results was obtained by averaging over 5×10^4 trajectories. The results marked by the asterisk were obtained by averaging over 10^4 trajectories. The relative errors of the former and latter do not exceed 2% and 4%, respectively.

Radii ratio a/R	Interpartition distance l/R					
	5	2	1	0.5	0.3	0.1
0.05	1.0*	0.99*	0.99*	0.98	0.97	0.75
0.1	0.99	1.0	1.0	0.99	0.94	0.63
0.3	1.0	0.99	0.99	0.96	0.87	0.46
0.5	1.0	0.99	0.98	0.96	0.87	0.48
0.7	1.0	0.99	0.99	0.98	0.94	0.63
0.9	1.0	1.0	0.99	0.99	0.98	0.95

given by Eqs. (5) and (6) with D_{eff} found numerically in Brownian dynamics simulations. (Trajectories were propagated using the standard Brownian dynamics algorithm, $\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \sqrt{2D\Delta t}\xi$, where $i = x, y, z$, and ξ is the Gaussian random number with zero mean, $\langle \xi \rangle = 0$, and unit variance $\langle \xi^2 \rangle = 1$. Whenever a trajectory crossed the boundary, the step was rejected and a new attempt was made.) The ratios of the two diffusion coefficients at different values of the aperture radius and the interpartition distance are given in Table I. One can see excellent agreement between the theoretical and simulation results at $l/R \geq 1$. The agreement is reasonably good at $l/R = 0.5$. The theory fails at smaller interpartition distances since boundary homogenization does not work under such conditions.¹⁶

III. TRANSIENT BEHAVIOR

As time goes from zero to infinity $D(t)$ monotonically decreases from D_0 to D_{eff} . To study transient behavior of the diffusion coefficient, we use the exact solution for the Laplace transform of $D(t)$ of a particle diffusing among periodically spaced permeable partitions found recently.⁹ The expression for $\hat{D}(s) = \int_0^\infty \exp(-st)D(t)dt$ given in Ref. 9 has a very complicated form. After some manipulations we managed to simplify this expression and found that the result obtained in Ref. 9 can be written in a much simpler form,

$$\hat{D}(s) = \frac{D_0}{s} \left(1 - \frac{1}{\sigma \coth \sigma + \tilde{P}} \right), \quad (7)$$

where $\sigma = (1/2)\sqrt{s l^2 / D_0}$ and $\tilde{P} = Pl/D_0 = 1/(\tau - 1) = (2l/\pi R)\nu f(\nu)$. As $s \rightarrow \infty$, Eq. (7) takes the form $\hat{D}(s) \approx D_0/s$, which shows that $D(t) \rightarrow D_0$ as $t \rightarrow 0$. In the $s \rightarrow 0$ limit, Eq. (7) leads to $\hat{D}(s) \approx D_{\text{eff}}/s$ that corresponds to $D(t) \rightarrow D_{\text{eff}}$ as $t \rightarrow \infty$.

It is convenient to describe transient behavior of $D(t)$ by means of the relaxation function $R(t)$,

$$R(t) = \frac{D(t) - D_{\text{eff}}}{D_0 - D_{\text{eff}}}, \quad (8)$$

which monotonically decreases from unity to zero as time goes from zero to infinity. Using this function $D(t)$ can be written as

$$D(t) = D_{\text{eff}} + (D_0 - D_{\text{eff}})R(t). \quad (9)$$

The Laplace transform of this relaxation function is

$$\hat{R}(s) = \frac{\hat{D}(s) - D_{\text{eff}}}{D_0 - D_{\text{eff}}}. \quad (10)$$

Using Eqs. (4) and (7) we can write $\hat{R}(s)$ as

$$\hat{R}(s) = \frac{\sigma \coth \sigma - 1}{s(\sigma \coth \sigma + \tilde{P})}. \quad (11)$$

In Fig. 3 we show the time course of the relaxation function at several values of the dimensionless permeability, \tilde{P} , which depends on both the radii ratio, $\nu = a/R$, and the ratio of the interpartition distance to the tube radius, l/R .

Based on the Laplace transform of the relaxation function, Eq. (11), one can find the relaxation time, t_{rel} , defined as

$$t_{\text{rel}} = \int_0^\infty R(t)dt = \hat{R}(0). \quad (12)$$

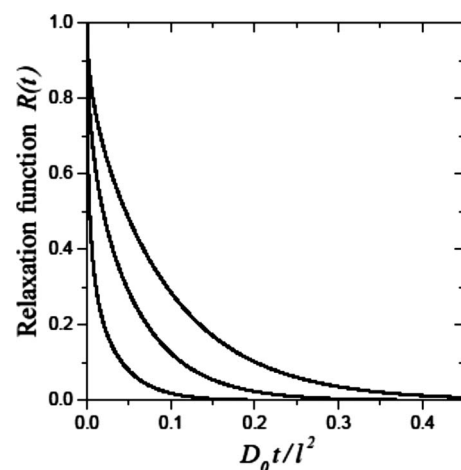


FIG. 3. Theoretically predicted time dependence of the relaxation function at three values of the dimensionless partition permeability, $\tilde{P} = Pl/D_0 = (2l/\pi R)\nu f(\nu)$, $\tilde{P} = 0.05, 1$, and 5 from top to bottom. The curves are obtained by numerically inverting the Laplace transform in Eq. (11). The relaxation accelerates as the permeability increases.

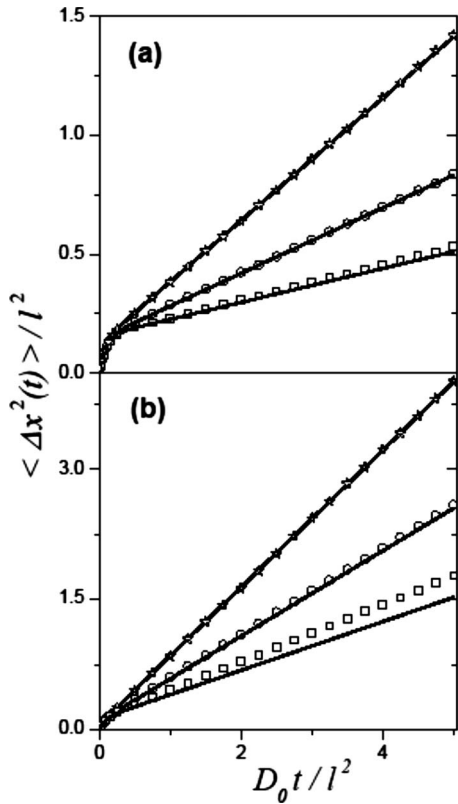


FIG. 4. The mean squared displacement as a function of time at two values of the radii ratio, $a/R=0.1$ [panel (a)] and $a/R=0.3$ [panel (b)]. Curves are theoretically predicted dependences obtained by numerically inverting the Laplace transform in Eq. (14). Symbols are the results obtained in Brownian dynamics simulations at $l/R=0.5$ (squares), $l/R=1.0$ (circles), and $l/R=2.0$ (stars). In simulations the results were obtained by averaging over 10^5 trajectories. The relative error of these results does not exceed 2%. One can see excellent agreement between theoretical and simulation results for all sets of the tube parameters except one, $a/R=0.3$ and $l/R=0.5$.

Using Eq. (11) we obtain

$$\frac{D_0 t_{\text{rel}}}{l^2} = \frac{1}{12(1 + \tilde{P})} = \frac{1}{12\tilde{P}\tau} = \frac{1}{12\left(1 + \frac{2l}{\pi R} \nu f(\nu)\right)}. \quad (13)$$

The relaxation time considered as a function of the radii ratio, ν , monotonically decreases as ν increases from zero to unity. This time vanishes as $\nu \rightarrow 1$ [tube with no partitions, $f(\nu) \rightarrow \infty$] and takes its maximum value as $\nu \rightarrow 0$. The latter is given by $l^2/(12D_0)$. It is interesting that the maximum relaxation time is well below the characteristic time of diffusive passage of the interpartition distance, l^2/D_0 . The relaxation time also depends on the interpartition distance, l . As might be expected, the relaxation time monotonically grows with l .

As an additional test of our approximate approach, in Fig. 4 we compare $\langle \Delta x^2(t) \rangle$ predicted theoretically and found in Brownian dynamics simulations at different values of the tube parameters. The theoretical dependences are obtained by numerically inverting the Laplace transform of $\langle \Delta x^2(t) \rangle$ given by

$$\langle \Delta x^2(s) \rangle = \frac{2}{s} \hat{D}(s) = \frac{2D_0}{s^2} \left(1 - \frac{1}{\sigma \coth \sigma + \tilde{P}} \right), \quad (14)$$

where we used the expression for $\hat{D}(s)$ in Eq. (7). At asymptotically large and small values of s , this Laplace transform takes the form

$$\langle \Delta x^2(s) \rangle = \frac{2D_0}{s^2} \times \begin{cases} 1, & s \rightarrow \infty, \\ \frac{\tilde{P}}{1 + \tilde{P}} + \frac{l^2 s}{12D_0(1 + \tilde{P})^2}, & s \rightarrow 0, \end{cases} \quad (15)$$

One can use this to find asymptotic behavior of $\langle \Delta x^2(t) \rangle$ as $t \rightarrow 0$ and $t \rightarrow \infty$,

$$\langle \Delta x^2(t) \rangle = \begin{cases} 2D_0 t, & t \rightarrow 0, \\ 2D_{\text{eff}} t + \frac{l^2}{6(1 + \tilde{P})^2}, & t \rightarrow \infty, \end{cases} \quad (16)$$

In Fig. 4 we show the mean squared displacement at $\nu=0.1$ [panel (a)] and $\nu=0.3$ [panel (b)]. In both panels we compare $\langle \Delta x^2(t) \rangle$ at $l/R=0.5$, 1.0 , and 2.0 . One can see excellent agreement between the theoretical and simulation results at $l/R=1.0$ and 2.0 at both $\nu=0.1$ and $\nu=0.3$. The situation is different at $l/R=0.5$. While there is a good agreement between the theoretical and simulation results at $\nu=0.1$, one can see the difference between the two at $\nu=0.3$. Note that at $l/R=0.5$ and $\nu=0.3$ the theory predicts D_{eff} with accuracy of 4%. As might be expected, the time dependence $\langle \Delta x^2(t) \rangle$ is a more sensitive indicator of the accuracy than D_{eff} , which is $\frac{1}{2}$ of the slope of the dependence $\langle \Delta x^2(t) \rangle$ at large times.

We also ran simulations and compared the results with the theoretical predictions at other values of the radii ratio (the results are not shown). At $\nu=0.5$ the situation is similar to that at $\nu=0.3$ [Fig. 4(b)], namely, while there is an excellent agreement between $\langle \Delta x^2(t) \rangle$ found in simulations and obtained by numerically inverting the Laplace transform in Eq. (14) at $l/R=1$ and 2 , there is an observable difference between the two at $l/R=0.5$. At smaller and larger values of the radii ratio ($\nu=0.05$, 0.7 , and 0.9) there is an excellent agreement between the theoretical and simulation results at all three values of the tube length.

IV. CONCLUDING REMARKS

In the present paper we developed a theory of diffusion in a tube with periodic partitions that separate the tube into compartments. Each partition has a circular aperture in its center, through which diffusing particles can go from one compartment to the other. The presence of partitions leads to slowdown of diffusion compared to that in the tube with no partitions. This slowdown manifests itself in variation of the time behavior of the mean squared displacement of the particle that changes from $\langle \Delta x^2(t) \rangle = 2D_0 t$ at very short times to $\langle \Delta x^2(t) \rangle = 2D_{\text{eff}} t$ as $t \rightarrow \infty$, where $D_{\text{eff}} = D_0/[1 + \pi R/(2l\nu f(\nu))]$ is smaller than D_0 . The main results of this paper are the expressions for the Laplace transforms of the time-dependent diffusion coefficient, Eq. (7), and of the

mean squared displacement, Eq. (14), which describe slow-down of diffusion. These expressions show how the slow-down depends on the parameters of the tube. Comparison of our theoretical predictions with the results of Brownian dynamics simulations demonstrates that the theory developed in the paper is applicable at arbitrary values of the radii ratio, $\nu = a/R$, when the tube radius does not exceed the interpartition distance, $l \geq R$.

The key step of our analysis is the replacement of non-uniform partitions with apertures by effective partitions that are uniformly permeable for diffusing particles. To choose the partition permeability, we use recently suggested expression for the effective trapping rate by a nonuniform partition in a cylindrical tube, which contains a perfectly absorbing circular disk in its center. This is boundary homogenization that is applicable when a diffusing particle has enough time to equilibrate its distribution over the tube cross section before it reaches the absorbing disk.

The condition of radial equilibration violates when the interpartition distance is smaller than the tube radius, $l < R$. In such geometry the theory fails since the pattern of the particle transitions between neighboring apertures changes. The point is that when $l < R$ there are two qualitatively different transition scenarios, fast and slow. In the fast scenario the transition time is relatively short, so that the particle goes from one aperture to the other without spending too much time outside the cylinder of radius a connecting the apertures. This is quite in contrast with how the interaperture transitions occur in the slow scenario, when the particle spends a huge amount of time traveling outside this cylinder. When the interpartition distance is large, the situation is different. In such a case the particle always has enough time to equilibrate over the tube cross section before reaching one of the two neighboring apertures. Thus, interaperture transitions show regular or intermittent behavior depending on whether the interpartition distance is larger or smaller than the tube radius. The theory developed in the paper is applicable in the former case and fails in the latter one.

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